METHODS FOR DETECTING ANALYTES USING CONJUGATED POLYMERS AND THE INNER FILTER EFFECT

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from U.S. Provisional Patent Application Ser. No. 62/955,764 filed Dec. 31, 2019. The entirety of the provisional application is incorporated herein by reference.

STATEMENT OF GOVERNMENT SUPPORT

[0002] This invention was made with government support under grant/contract number OIA-1632825 awarded by the National Science Foundation. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The methodology disclosed relates to chemical sensing and novel methods and processes for detecting diverse analytes and mixtures of analytes. The methods utilize π-conjugated polymers with controlled optical properties to detect and discriminate analytes through the inner filter effect and data processing techniques.

SUMMARY OF THE INVENTION

[0004] The methods and processes provide for utilizing π-conjugated polymers with controlled optical properties for the detection of small molecule, macromolecular, and biological analytes. The chemical sensors operate through an inner filter effect due to the similar optical properties of the π-conjugated polymers and analytes. Data analysis may proceed via multivariate techniques, allowing for the discrimination of similar and different analytes. The novel methodologies provide approaches for the detection, discrimination, and quantification of both individual and mixtures of optically active analytes in various chemical environments.

BACKGROUND OF THE INVENTION

[0005] Solution-processable organic semiconductors based on small molecules and polymers have provided a new generation of optoelectronic technologies owing to their modularity, distinct manufacturing paradigms, diverse optical and transport properties, and opportunities for innovation not possible using inorganic materials. Significant technological milestones have been achieved such as commercially available organic light emitting diodes, infrared photodetectors that do not require cryogenic cooling, printed electronic devices, biocompatible medical materials, and sensing technologies that were previously unimaginable. Organic semiconductor-based sensors utilize fluorescent conjugated polymers (CPs) and conjugated polyelectrolytes (CPEs) which can simultaneously function as molecular recognition and signal transduction elements for analyte detection, which display unique signal amplification characteristics when compared to small molecule sensors, leading to orders of magnitude improvements in sensitivity. For example, the modularity, stability, and low detection limits of these systems are ideal for applications in food and water quality monitoring, medical analysis, environmental monitoring, precision agriculture, etc. Widespread interest in CP sensing technologies has further motivated research efforts aimed at expanding the scope and sensitivity of these materials and technologies. CPs transduce signals through the migration of excitons which are relatively immune to electrostatic and dielectric variations, allowing their successful implementation for sensing applications within complex environments. The diffusing exciton is captured through binding events along the polymer, resulting in the collective response of each repeat unit within the exciton diffusion length. The exciton diffusion process and correlated optical response are closely related to the electronic and structural conformation of the polymer backbone, which can be synthetically tuned to incorporate molecular design features that enhance exciton delocalization, leading to stronger amplified signals and low limits of detection. These mechanisms are distance dependent and require CP-analyte interactions that are facilitated through the incorporation of receptors within, or extended from, the CP backbone. The lack of specific recognition elements for challenging analytes, and of electronically coupling analyte-receptor interactions into transducible optical responses, complicates the development of optical sensing platforms capable of profiling many analytes in complex mixtures. These downfalls are fundamentally associated with the nature of signal transduction typically employed within CP-based sensing platforms.

[0006] More recently, array-based sensing has been used to profile combinations of structurally and chemically similar analytes through multivariate pattern recognition. Subtle structural differences between nonspecific CP-based sensors allow for differential interactions with analytes that establish identifying optical responses, which creates a "chemical fingerprint" used to discriminate similar compounds using pattern recognition algorithms to highlight and summarize distinguishing features in large data sets leading to chemical differentiation. Current array-based CP sensors utilize traditional analyte-driven responses requiring complex recognition elements, thereby limiting their scope.

[0007] The inner filter effect (IFE) results from the absorption of light by a chromophore in solution, preventing photons from reaching a fluorophore, creating an observed decrease in fluorescence emission. Sensing platforms operating through the IFE rely on the spectral overlap between the sensor and the analyte rather than traditional host-guest chemistries, circumventing the need for tailored receptors. CP-based sensors have been recently reported utilizing the IFE for the detection of contaminants, however the use of the IFE alone is nonspecific and does not allow for the differentiation of similar analytes.

[0008] Despite the advantages and vast number of reports in the sensing literature using CPs, the advantages of both array-based sensing and the IFE have not been leveraged in CP-based sensors. Sensors and a system that utilize the unique signal transduction of the IFE, coupled with machine-learning data processing, would address the problems associated with CP-based sensors. The methodology described herein provides such solutions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] In the accompanying drawings:
[0010] FIG. 1 shows the synthesis and chemical structures of the conjugated polymers P1-P3.
[0011] FIG. 2 shows a graphical representation of the UV-Vis absorption spectrum of polymer P2 and Acid Red (AR) 112.